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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE April 6, 1999		3. REPORT TYPE AND DATES COVERED Technical Report
4. TITLE AND SUBTITLE Preliminary Complexation Studies of Bis-(8-Hydroxyquinoline)-substituted Tetraaza-15-crown-5 with Various Metal Ions			5. FUNDING NUMBERS N00014-98-1-0485 98PR05020-00	
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry and Biochemistry Brigham Young University Provo, UT 84602			8. PERFORMING ORGANIZATION REPORT NUMBER Technical Report No. 7	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Dr. Kelvin Higa (Program Director) Office of Naval Research 800 No. Quincy Street Arlington, VA 22217-5000			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Complexation of bis(8-hydroxyquinoline)-substituted tetraaza-15-crown-5 (1) (see our Technical Report No. 6) with Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} was evaluated potentiometrically in aqueous solution (0.10 M Me_4NCl) at 25°C. Ligand 1 formed very stable complexes with these metal ions. The UV-Vis spectra of 1 and its complexes were examined in an aqueous acetic acid buffer solution (pH 4.7). The 1- Cu^{2+} complex provided a new absorption band at 258 nm.				
14. SUBJECT TERMS			15. NUMBER OF PAGES	
			16. PRICE CODE NA	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited	

OFFICE OF NAVAL RESERACH

Grant N00014-98-1-0485

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**Preliminary Complexation Studies of Bis(8-hydroxyquinoline)-substituted
Tetraaza-15-crown-5 with Various Metal Ions**

by

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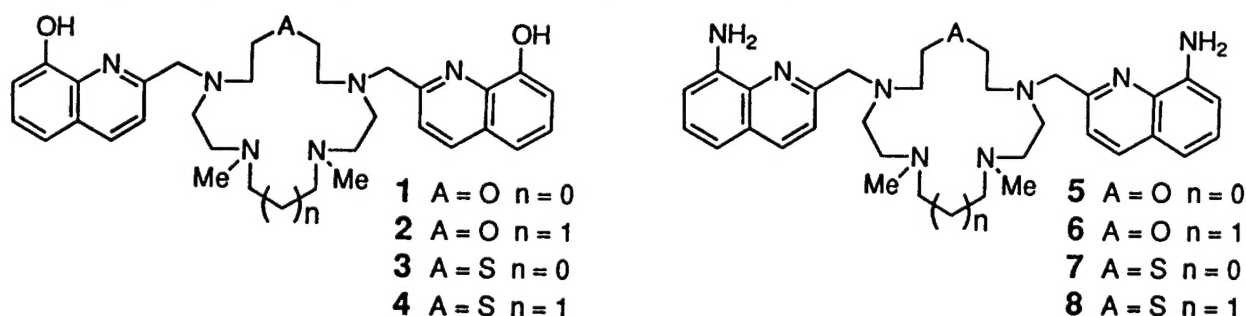
PRELIMINARY COMPLEXATION STUDIES OF
BIS(8-HYDROXYQUINOLINE)-SUBSTITUTED TETRAAZA-
15-CROWN-5 WITH VARIOUS METAL IONS

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Results and Discussion

A series of new 8-hydroxyquinoline- and 8-aminoquinoline-substituted tetraaza-15-(-16)-crown-5 ethers (1-4 and 5-8, respectively) have been prepared in our laboratory.¹ These new ligating agents were designed to selectively bind transition and post-transition metal ions with a concomitant modulation in the absorption and fluorescent spectra of the compounds. This report gives a preliminary account of the complexation of ligand 1 with various metal ions.



Protonation and Complexation Studies of Ligand 1. Protonation constants of 8-

hydroxyquinoline-containing tetraazacrown ether 1 and stability constants for the interactions of 1 with Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} were determined by a potentiometric titration technique² at 25°C in aqueous solution. The ionic strength was kept constant with 0.10 M tetramethylammonium chloride. The overall reactions are expressed by the general equation:



where M is the metal ion and L is the ligand. The overall equilibrium constant can be defined as

$$\beta_{pqr} = [\text{M}_p\text{H}_q\text{L}_r^{(2p+q-2r)}] / [\text{M}^{2+}]^p [\text{H}^+]^q [\text{L}^{2-}]^r \quad (2)$$

The values of the protonation constants of the ligands and stability constants of the metal ion complexes ($\log \beta_{pqr}$) are listed in Tables 1 and 2, respectively.

Four protonation constants can be calculated for compound 1. The first two protonation constants ($\log K_1 = 9.55$ and $\log K_2 = 7.30$ (16.85 - 9.55), Table 1) and the last two constants

Table 1. Logarithms of Protonation Constants of Macrocyclic Ligand 1 in Aqueous Solution (0.10 M Me₄NCl) at 25.0 °C

Reaction	log β
$H^+ + L^{2-} \rightleftharpoons HL^-$	9.55 ± 0.05
$2H^+ + L^{2-} \rightleftharpoons H_2L$	16.85 ± 0.08
$3H^+ + L^{2-} \rightleftharpoons H_3L^+$	19.87 ± 0.09
$4H^+ + L^{2-} \rightleftharpoons H_4L^{2+}$	21.31 ± 0.14

(log $K_3 = 3.02$ and log $K_4 = 1.44$) are close to each other. A large decrease in protonation constants is seen between the second and the third protonation steps. Since the first protonation constant of 1 (log $K_1 = 9.55$) is hydroxyquinoline (9.65 at 25 °C, $\mu = 0.1$),³ the first two protonation constants of 1 are due to protonation of OH groups of the 8-

hydroxyquinoline portion and the last two forming a neutral complex with a divalent cation which may be coordinated by both the 8-hydroxyquinolines and the macroring.

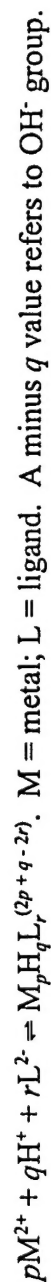
Data in Table 2 show that each metal ion studied forms several types of complexes with the ligand. The 1:1 complexes ML ($p = 1, q = 0, r = 1$ in eq. 1) and M(OH)L⁻ ($p = 1, q = -1, r = 1$) are observed in each case. The complexes of ligand 1 with Cu²⁺, Co²⁺, Ni²⁺, Zn²⁺, Cd²⁺, and Pb²⁺ are very stable in aqueous solution. The large stability constants (log $\beta_{ML} > 12$ and log $\beta_{MHL} > 15$) are shown in Table 2. The most stable complexes were observed for Cu²⁺. The values of log β_{CuL} and log β_{CuHL} are 15.5 and 18.6, respectively. Cd²⁺ also forms very stable complexes with ligand 22 (log $\beta_{CdL} = 15.3$ and log $\beta_{CdHL} = 17.5$). Therefore, not only the fully deprotonated form of 22 (L²⁻) but also the monoprotonated ligand (HL⁻) forms very stable complexes with the metal ions studied (except for Co²⁺). In the case of Co²⁺, the complex CoHL⁺ was not detected. However, Co²⁺ forms a 1:2 (M:L) complex with 1 (log $\beta_{CoL_2} = 20.2$). A dinuclear complex with Cu²⁺, Cu₂L²⁺, was also observed. The equilibrium constants of the complexes containing hydrolysis products of the metal ions, M(OH)L⁻, range from 6.44 (log $\beta_{Co(OH)L}$) to 9.62 (log

Table 2. Overall Stability Constants^a of Metal Ion Complexes with Macrocyclic Ligand 1 in Aqueous Solution (0.10 M Me₄NCl) at

25.0 °C

			$\log \beta_{pqr}$				
<i>p</i>	<i>q</i>	<i>r</i>	Cu ²⁺	Co ²⁺	Ni ²⁺	Zn ²⁺	Pb ²⁺
1	0	1	15.52 ± 0.08	12.34 ± 0.04	13.46 ± 0.03	12.41 ± 0.03	15.33 ± 0.02
1	1	1	18.55 ± 0.12		16.15 ± 0.18	15.55 ± 0.09	17.50 ± 0.05
1	-1	1	8.53 ± 0.19	6.44 ± 0.06	7.49 ± 0.12	6.49 ± 0.05	9.62 ± 0.07
2	0	1	18.92 ± 0.22				
1	0	2		20.19 ± 0.06			
1	-2	1			-3.59 ± 0.25		

^aThe equilibria of the reactions are defined by the general equation:



$\beta_{\text{Cd(OH)L}}$). The Ni^{2+} forms a second type of hydrolysis complex, $\text{Ni(OH)}_2\text{L}^{2-}$, which has a very low equilibrium constant (Table 2).

UV-Visible spectra. The UV spectra of free and complexed ligand 1 are shown in Figures 1 and 2. The free 1 has an absorption maximum at 244 nm. Upon addition of Cu^{2+} , a new peak develops at 258 nm (Figure 1). Other metal ions (Zn^{2+} , Pb^{2+} , Cd^{2+} , Ag^+ , Hg^{2+} , Co^{2+} , and Ni^{2+}) were also titrated with 1, but none produced a new peak or significantly interfered with the new 1- Cu^{2+} complex peak at 258 nm (Figure 2). Thus, the 258 nm peak for the 1- Cu^{2+} complex could be used for sensing purposes.

Experimental Section

Determination of Protonation and Stability Constants. The protonation and stability constants were determined by potentiometric titration in aqueous solution at 25 °C. The titrations were carried out at a constant ionic strength of 0.10 M Me_4NCl using an automatic microprocessor-controlled potentiometric titrator.⁴ Temperature was controlled within ± 0.1 °C using a jacketed cell through which water from a constant-temperature bath was circulated. Potentials to within ± 0.1 mV were measured using an Orion Model 701A Digital Ion Analyzer in conjunction with a Cole-Parmer combination electrode (Ag/AgCl reference cell). The electrode was calibrated by two precision buffer solutions, pH 4.000 ± 0.002 and 7.000 ± 0.002 at 25.0 °C (Cole-Parmer). Calculations were performed with the SUPERQUAD program⁵ using an IBM computer. Compound 1 was used as its adduct with HCl ($1 \cdot 6\text{HCl}$) which had good solubility in aqueous solution (0.01 M).

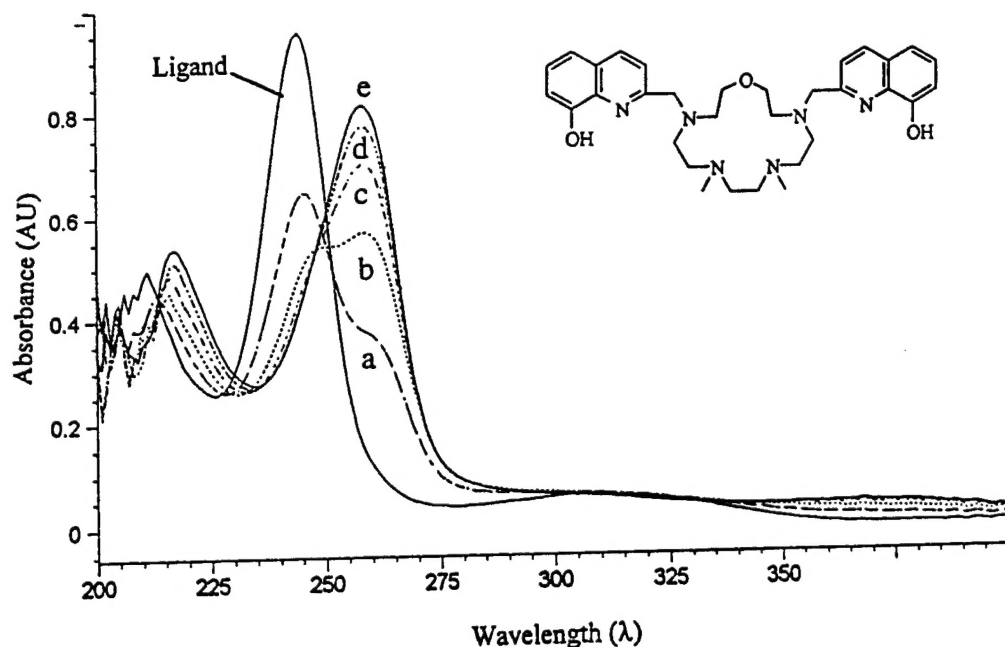


Figure 1. UV-visible spectra of free 1 and its Cu^{2+} complexes in an aqueous buffered solution. $[1] = 0.977 \times 10^{-5} \text{ M}$, $[\text{buffer}] = 5.0 \times 10^{-2} \text{ M}$ acetic acid ($\text{pH} = 4.7$). The labels a - e indicate 1 - 5 equivalents of Cu^{2+} added to the ligand successively.

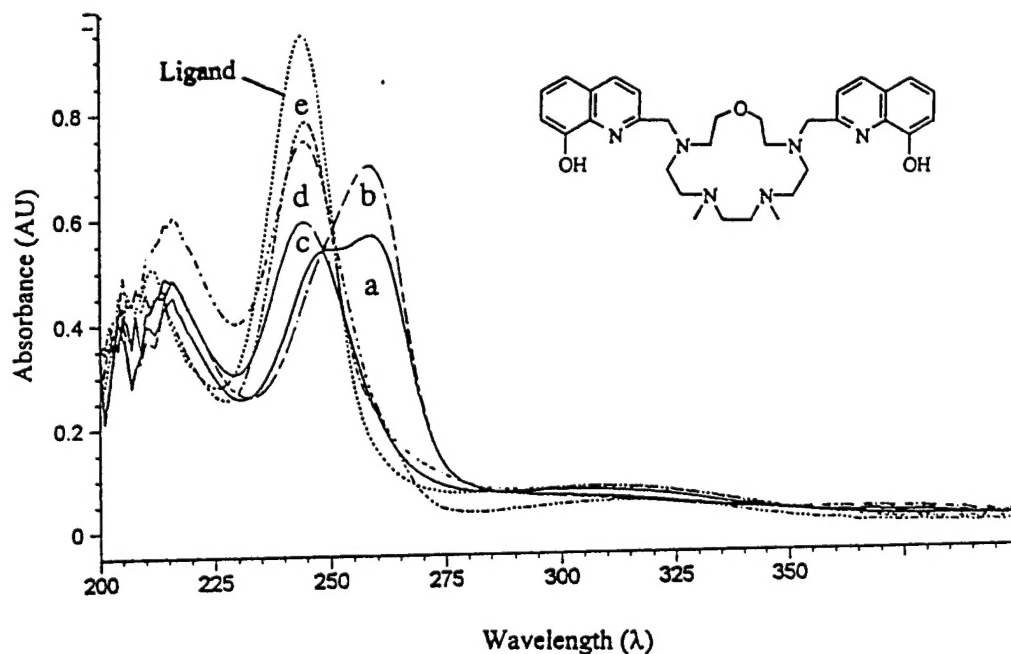


Figure 2. UV-visible spectra of free and complexed 1 in acetic acid buffer solution ($\text{pH} = 4.7$). (a and b) Cu^{2+} (1 and 2 equivalents, respectively), (c) Zn^{2+} , (d) Pb^{2+} , and (e) Cd^{2+} (2 equivalents each). $[1] = 0.977 \times 10^{-5} \text{ M}$ and $[\text{buffer}] = 5.0 \times 10^{-2} \text{ M}$ acetic acid.

UV-visible Spectral Measurements. UV-visible spectra were recorded at 23 ± 1 °C in a 1-cM quartz cell using a Hewlett-Packard 8452A Diode Array spectrophotometer. Both ligand and metal ions were prepared in aqueous acetic acid buffer (pH = 4.7). Concentrations of acetic and sodium acetate were 5.00×10^{-2} M and 5.00×10^{-2} M, respectively, and concentration of ligand 1 was 1.00×10^{-5} M. The metal ion concentrations were 1-5 times the ligand concentration.

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